

HYDROCONVERSION OF COAL AND CARBONACEOUS MATERIALS USING DISPERSED SLURRY CATALYSTS

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Abstract

Hydrocarbon Technologies, Inc. (HTI) working with the U.S. Department of Energy has developed hydroprocessing technologies, such as HTI Coal™, HTI CoPro™, and HTI CoPro Plus™, for catalytic hydroconversion of coal, petroleum residual, organic wastes, and mixtures thereof into value-added products, including liquid transportation fuels and chemical feedstocks. These hydroconversion processes are based upon the use of specific catalysts including a novel iron-based catalyst in a gel form, HTI GelCat™, to catalyze hydrogenation and cracking reactions of carbonaceous feeds. HTI GelCat™ is a dispersed, fine-sized, anion-modified iron oxide catalyst which may also be promoted by other elements. In the dried form, this catalyst has a high surface area exceeding about 100 m²/g and a primary particle size smaller than about 50 Angstrom. The gel form of the catalyst is typically used for hydroconversion reactions at 5000 or less ppm of iron and 100 or less ppm of the other promoter metals relative to the feed material. The catalyst in the gel form, upon entering the high temperature reactor, explodes into very fine sized, high surface area particles due to the rapid evaporation of water in the gel.

Catalytic hydroconversion processes utilizing the HTI GelCat™ can be conducted in a single-stage reactor, but preferably in two-stage reactors connected in series, with or without interstage separation. Reaction conditions for petroleum residuum hydroconversion are usually 425-450°C in temperature and 7-17 MPa in hydrogen partial pressure. Under these conditions, large molecules are cracked, hydrogen is added and sulfur, nitrogen, and chlorine, etc. are readily removed and recovered after conversion to their basic hydrogenated form. During the past year, HTI has conducted several successful bench scale tests under DOE Proof of Concept Program (PB-05, 06, and 07). Results indicate that, in coprocessing of coal, petroleum resid and plastics, total feed conversion as high as 99 W% can be achieved. Resid (524°C+) conversion and distillate yield exceed 84 and 76 W%, respectively. For direct coal liquefaction, the coal conversion of as high as 97 W% can be achieved. The use of HTI GelCat™ makes the coprocessing processes very flexible in selection of various feedstocks. Extremely significant to the coprocessing process performance is the effect of plastics addition on the hydrogen consumption. Not only does the addition of plastics to the oil only operation or coal/oil operation improve process performance, but also reduce the hydrogen consumption remarkably. This paper reviews results obtained from the direct coal liquefaction and waste-coal coprocessing runs completed in 1996-1997.

Preliminary economic studies have been conducted based on the construction of a fully-integrated grass-roots commercial coal/oil/plastics co-liquefaction complex, employing HTI GelCat™ to manufacture finished gasoline and diesel fuel products. The co-processing of coal, oil and plastics has achieved an extremely low equivalent crude oil price of \$19.64/barrel, showing a promising economic viability towards commercialization.

Introduction

HTI has a continuing program on the multi-stage catalytic processing of sub-bituminous and bituminous coals. The goal of this program, sponsored by the U.S. DOE/ FETC, is to develop further the technology and process for the production of premium liquid fuels from the direct liquefaction of coal in an environmentally acceptable manner. The coal-derived liquids should be economically competitive with petroleum. The majority of experimentation is conducted on a 50 kg/day continuous pilot-scale unit that can be configured as a single-, two-, and three-stage reactor system. The liquefaction reactor can be operated in ebullated or expanded bed mode, or slurry-bed mode. The unit is equipped with interstage sampling, interstage separation, in-line hydrotreating and alternative bottoms separation devices. Several reactor configurations and catalyst combinations have been studied over the last several years. These configurations include the following: ebullated or expanded bed reactors using supported Ni/Mo catalysts, combinations of dispersed catalysts and supported catalysts (Hybrid Mode), i.e., no supported catalyst in the one stage and an all dispersed catalyst back-mixed reactor in the other stage and an all slurry two stage reactor mode.

Operating variables were temperature, time and catalyst concentration. Emphasis has been placed on using low cost, unsupported, fine particle size (5-10nm) catalysts in slurry back-mixed reactors.

Due to the high activity of these dispersed iron-based catalyst, they can be used in low concentration of iron (0.1-0.5 W% iron relative to feed) for various hydrogenation and hydroconversion reactions mentioned above, and are preferably recycled with the unconverted or partially converted high boiling fraction (454°C+) back to the reactor for further reaction. Because these fine-sized iron catalysts are produced from relatively inexpensive and environmentally friendly materials. The catalyst is usually disposable for large scale process and does not require recovery and regeneration.

Experimental

Pilot scale tests were carried out at the pilot plant described previously. The coal, oil, waste materials and HTI Gel Cat™ catalyst were premixed in a mixing tank prior to charging to the Feed Tank. Joined by feed hydrogen, the gas/feed slurry stream passed through a short residence time coiled preheater. Reaction was conducted at 15MPa of hydrogen, 400-460°C and 1000-5000 ppm of Fe catalyst loading. An internal circulating pump returned a portion of the reactor slurry to the bottom of the reactor continuously providing the backmixing action. The first-stage effluent was separated in the interstage separation, and the overhead light product, along with other second stage non-hydrotreated products, were fed to the direct-coupled hydrotreater. The interstage bottom stream was further liquefied in the second stage backmixed reactor.

The hot vapor products from the second stage liquefaction reactor were separated in the hot separator and fed directly into a fixed bed hydrotreater, which was connected directly with the hot separator without pressure reduction. Hydrogen, C₁-C₃ hydrocarbons, heteroatom gaseous products, water and volatile liquid products from the overhead of the separator passed through a mixing phase trickled bed hydrotreater. The main function of the hydrotreater was to stabilize the hydrocarbon products and to reduce heteroatom (N,S,and O) content.

The backend separation included pressure filtration and vacuum distillation. The major net product streams are product gases (1st and 2nd stages), dissolved gas (2nd stage only), 2nd stage hydrotreated product and toluene extracted solids and excess pressure filter liquid (PFL) or vacuum still overhead (VSOH). Process performance is determined by feed composition, operating conditions, yield and quality of C₄-524°C distillate, and hydrogen utilization efficiency.

Results and Discussion

Assumption and Basis of Economic Evaluation

The process performance and economic evaluation obtained from recent pilot scale co-processing operations are discussed in this paper. The economic evaluation studies were based on construction of a fully-integrated grass-roots commercial coal/oil/waste (plastics) co-liquefaction complex to manufacture finished gasoline and diesel fuel liquid products. The co-liquefaction plant in the complex is a multi reactor-train facility and the total feed processing capacity has been selected assuming the construction of maximum-sized heavy-walled pressure vessels to carry out the co-liquefaction reactions. Coal and waste plastics required in the co-liquefaction plant are prepared on site and storage is provided for the oil received. Unconverted feed plus residual oil from the co-liquefaction are gasified to meet a part of the hydrogen requirements of the complex.

Part of the fuel requirement is met by the waste process gases. Natural gas is imported to meet the remaining fuel requirements and to satisfy the remainder of the hydrogen requirements. The costs and operating requirements of the other process facilities and the off-sites have been estimated from the Bechtel Baseline Design Study. The most significant criterion reported is the equivalent crude oil price. This concept was developed by Bechtel in their Baseline Design Study, and modified slightly for use in this study.

Waste-Coal Co-processing Using HTI GelCat™

Table 2 presents the comparisons of the performance of five run conditions. Coprocessing of Black Thunder coal, Hondo oil and ASR (Auto Shredder Residue) resulted in 83.6 W% resid conversion and 66.8 W% distillate yield. A dramatic drop in both resid conversion and distillate yield was observed when Hondo oil was removed from the mixture of coal and ASR(PB-04-4). It seemed that vehicle solvent is essential in converting ASR and coal. In Run PB-04-5, 25 W% of plastics was added to the coal and ASR mixture, it is interesting to note that distillate yield was increased from 56.6 to 61.4 W% while 524°C+ resid conversion was increased proportionally, from 72.4 to 77.2 W%. Also, it is observed that addition of plastics has a significant impact on hydrogen consumption. Not only does the addition of plastics to coal/ASR improved the process performance, but also reduce hydrogen consumption by about 2 W%. Economical analysis showed that by adding plastics to coal/ASR feedstock, equivalent crude oil price dropped by \$6/barrel.

It was concluded that auto-fluff, that contains primarily polyurethanes and high impact polystyrene as its principal polymeric constituents and high ash levels, was not as effective as the curbside plastics in improving the coal hydroconversion process performance, i.e. auto-fluff was not found to either increase the light distillate yields or decrease the light gas make and chemical hydrogen consumption in coal liquefaction, in the manner done by curbside plastics

In Run PB-06, waste plastics was pretreated by pyrolysis and only 343 °C+ pyrolysis oil was coprocessed with coal and Hondo oil. As shown in *Table 2*, in Run PB-06-3, performance of coprocessing of coal/Pyrolysis oil, in terms of distillate yield and resid conversion, was similar to coprocessing of coal/ASR (PB-04-4), slight decrease in hydrogen consumption was observed. Considering Mo catalyst was not used in Run PB-06-03, this result seemed to suggest that plastics pyrolysis oil was more reactive in improving coal conversion than ASR. Run PB-06-4, using a mixed feed of coal, Hondo oil and pyrolysis oil, was performed at a much higher space velocity. Distillate yield and 524°C+ resid conversion was decreased by 3 and 7 W%, respectively. However, C₁-C₃ light gas yield and hydrogen consumption decreased dramatically. Results from Run PB-06-4 demonstrated the potential for commercialization because the equivalent crude price dropped to \$ 19.6/barrel.

Reactivity of Subbituminous Coal and Bituminous Coal In Waste-Coal Coprocessing

Table 3 illustrated the comparison of co-processing performance using different coals. In comparing the same feed mixture, Illinois #6 coal (Run PB-05-4) appeared to be more reactive than Black Thunder coal (Run PB-06-2), as both the distillate yield and resid conversion were higher. However, the use of Illinois #6 coal resulted in higher hydrogen consumption under the same conditions. Significant improvement was observed when part of the coal in Run PB-05-4 was replaced by Hondo Oil (PB-05-3).

The liquid products from these co-processing operations were clean and good feedstocks for refining operations. For these distillates, heteroatoms could be easily reduced if needed. These distillates from coprocessing of oil, plastics and coal can make acceptable blendstocks for diesel and jet fuel due to their high cetane number (42-46) and high naphthenes (over 50 v%) content. The superior quality of distillate products from HTI's coprocessing runs (attributable to the in-line hydrotreating operation and added components from coprocessing) yield an estimated a three-dollar premium over neat petroleum liquids.

Performance of HTI GelCat™ in Direct Coal Liquefaction

Bench run PB-07 was designed to evaluate the effects of varying levels of iron and promoters loading on liquefaction of a high volatile bituminous Illinois No.6 coal. The results are summarized in *Table 1*. Coal conversions were very high (96-97 W%) and so were the resid conversions (87-89 W%). With about 2500 ppm iron, employed as GelCat™, and under prevailing reaction conditions, neither molybdenum nor promoter 1 were found to have any significant impact on the overall process performance. This is mainly due to the loss of hydrogenation function at high temperatures. Substantial hydrocracking was observed during this run, as exemplified by the abnormally high gas yields(15-16 W%). In the absence of iron based GelCat™, even with Molyvan A and promoter 1, the resid levels in the recycle solvent increased up to 50 W%, creating significant pumping problems and forcing a premature unit shut-down.

Ongoing Bench Test-Co-processing of Pyrolysis Oil and Coal

Bench run PB-08 has been designed to study the processing of oils derived from mild pyrolysis of scrap tires, waste plastics, and waste lube oils to obtain the data required for economic comparisons with DOE database. The pyrolysis technology acquired is versatile and competitive and can also be used to pyrolyze other carbon-based waste materials. The heavy, high sulfur oils derived from pyrolysis can be processed along with coal and waste plastics in the direct liquefaction process. The Bench run PB-08 will be completed by the end of August, 1997.

Conclusion

Co-processing of waste with oil and coal using HTI's technology resulted in enhanced 524°C+ resid conversion and distillate yield. Economical evaluation has shown that co-processing of plastics with oil, coal or their mixture reduced the equivalent crude oil price to a competitive level. This puts the technology in the reach of immediate commercialization with either a small increase in world oil prices, government tax relief incentives or minor improvements in the technology to further reduce the product cost.

Table 1: Performance of HTI GelCat™ in Coal Liquefaction					
Run ID	PB-07-1	PB-07-2	PB-07-3	PB-07-4	PB-07-5
Feed Coal	Illinois#6	Illinois#6	Illinois#6	Illinois#6	Illinois#6
Catalyst					
Fe GelCat™	2500	2500	2500	0	2500
Promoter 1	250	100	100	100	0
Molyvan A	0	33	100	100	0
Temperature, °C					
K-1	449	449	449	449	449
K-2	460	460	460	460	460
Space Velocity					
(kg/h/m ³)	640	640	640	640	640
Performance					
Feed Conversion	96.3	97.0	96.3		96.4
C ₄ -524°C Yield	69.0	71.1	67.0		68.1
524°C+ Conv.	87.1	86.0	87.5	N/A*	88.8
C ₁ -C ₃ Gas Yield	14.6	11.9	15.1		16.2
H ₂ Consumption	7.9	8.6	7.5		8.3

* Condition 4 could not be completed as planned due to the plugging problems caused by the absence of Fe catalyst.

Table 2: Performance of Coal/Waste Coprocessing Using GelCat™

Run ID	PB-04-3	PB-04-4	PB-04-5	PB-06-3	PB-06-4
Feed Comp.W%	Coal/Oil/ASR	Coal/ASR	Coal/ASR/PLS	Coal/Pyr. Oil	Coal/Oil/Pyr
Coal	50	75	50	67	45
(Black Thunder)					
Hondo Oil	30				28
Plastics			25		
ASR	20	25	25		
343°C+ Pyr. Oil				33	27
Catalyst					
Fe GelCat™	1000	1000	1000	1000	1000
Mo	50	50	50	0	0
Space Velocity					
(kg/h/m ³)	602	632	621	655	1356
Performance					
(W% maf feed)					
Conversion	94.1	90.5	91.3	91	86
C ₄ -524°C Yield	66.8	56.6	61.4	57	54
524°C+ Conv.	83.6	72.4	77.2	73	66
C ₁ -C ₃ Gas Yield	8.6	6.9	7.8	8.8	3.5
H ₂ Consumption	5.7	6.0	4.0	5.4	2.2
Economic Comparison (12,000 Tons/Day Total Feed)					
Feed Rate, T/D					
Coal	6000	9000	6000	8040	5400
Hondo Oil	3600				3360
Plastics			3000		
ASR	2400	3000	3000		
343°C+ Pyr Oil				3960	3240
Liquid Prod, B/D					
Gasoline	13196	10141	12205	11527	10310
Diesel Fuel	32048	24629	29641	41238	35875
Total Investment					
(\$MM)	2680	2654	2644	2734	2852
Operating Cost					
(\$MM/Yr)	583.6	519.5	561.9	505.2	639.9
Eq. Crude Oil,\$/b	30.34	36.25	28.99	23.41	19.64

ASR=Auto Shredder Residue

PLS=Plastics

Pyr Oil=Pyrolysis Oil

Table 3: Performance of Coal/Waste Coprocessing Using Different Feed Coals

Run ID	PB-04-5	PB-06-2	PB-05-3	PB-05-4	PB-05-5
Feed Comp.W%	Coal/ASR/PLS	Coal/PLS	Coal/Oil/PLS	Coal/PLS	Coal/ASR/PLS
Coal (Black Thunder)	50	67			
Coal (Illinois # 6)			33	67	67
Hondo Oil			33		
Plastics	25	33	33	33	17
ASR	25				16
343°C+ Pyr. Oil					
Catalyst					
Fe GelCat™	1000	1000	1000	1000	1000
Mo	50	0	50	50	50
Space Velocity (kg/h/m ³)	621	560	579	669	758
Performance (W% maf feed)					
Conversion	91.3	91	99.1	97.1	96.2
C ₄ -524°C Yield	61.4	59	78.8	74.6	72.4
524°C+ Conv.	77.2	75	89.6	84.3	81.6
C ₁ -C ₃ Gas Yield	7.8	7.9	9.0	8.2	7.1
H ₂ Consumption	4.0	3.9	3.9	5.4	5.8
Economic Comparison (12,000 Tons/Day Total Feed)					
Feed Rate, T/D					
Coal	6000	8040	4000	8040	8040
Hondo Oil			4000		
Plastics	3000	3960	4000	3960	2040
ASR	3000				1920
343°C+ Pyr Oil					
Liquid Prod, B/D					
Gasoline	12205	12305	16201	14354	13645
Diesel Fuel	29641	29885	39346	34860	33137
Total Investment (\$MM)	2644	2469	2450	2449	2551
Operating Cost (\$MM/Yr)	561.9	446	514.3	486.3	515.9
Eq. Crude Oil,\$/b	28.99	26.19	22.43	24.20	25.20

